Effect of graphene substrate on the SERS Spectra of Aromatic bifunctional molecules on metal nanoparticles

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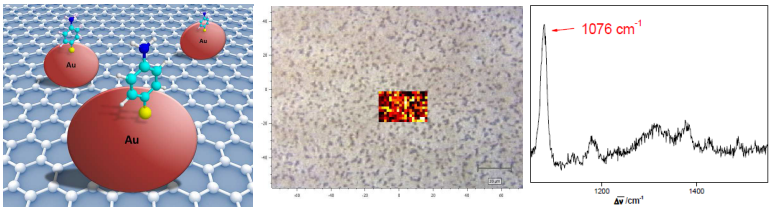
The design of molecular sensors plays a very important role within nanotechnology and especially in the development of different devices for biomedical applications. Biosensors can be classified according to various criteria such as the type of interaction established between the recognition element and the analyte or the type of signal detection from the analyte (transduction). When Raman spectroscopy is used as an optical transduction technique the variations in the Raman signal due to the physical or chemical interaction between the analyte and the recognition element has to be detected. Therefore any significant improvement in the amplification of the optical sensor signal represents a breakthrough in the design of molecular sensors. In this sense, *Surface-Enhanced Raman Spectroscopy* (SERS) involves an enormous enhancement of the Raman signal from a molecule in the vicinity of a metal surface.
The main objective of this work is to evaluate the effect of a monolayer of graphene oxide (GO) on the distribution of metal nanoparticles (NPs) and on the global SERS enhancement of p-aminothiophenol (pATP) and 4-mercaptobenzoic acid (4MBA) adsorbed on this substrate. These aromatic bifunctional molecules are able to interact to metal NPs and also they offer the possibility to link with biomolecules. Additionally by decorating Au or Ag NPs on graphene sheets, a coupled EM effect caused by the aggregation of the NPs and strong electronic interactions between Au or Ag NPs and the graphene sheets are considered to be responsible for the significantly enhanced Raman signal of the analytes [1-2]. Since there are increasing needs for methods to conduct reproducible and sensitive Raman measurements, *Graphene-enhanced Raman Scattering* (GERS) is emerging as an important method [3].



The Raman mapping analysis of the GO substrate has revealed a more homogeneous distribution of metal NPs with respect to the direct deposition of metal NPs on glass which favours the reproducibility of the SERS substrates. On the other hand, pATP and 4MBA have been shown a weaker adsorption capability on the graphene sheets and only bind to Au or Ag NPs, so the whole Raman spectra can be considered an overlapping of the spectra of these molecules and those of graphene enhanced by the Au or Ag NPs individually.

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References
[1] J. Huang, L. M. Zhang, B. A. Chen, N. Ji, F. H. Chen, Y. Zhang, Z. J. Zhang, *Nanoscale* **2**, 2733–2738 (2010).
[2] Y. Wang, Z. Ni, H. Hu, Y. Hao, C. P. Wong, T. Yu, J. T. L. Thong, Z. X. Shen, *Appl. Phys. Lett.* **97**, 163111–163113 (2010).
[3] F. Yaghobian, T. Korn, C. Schller, *Chem. Phys. Chem.* **13**, 4271 – 4275 (2012).